

# Surface Tension of Molten Zinc Borates

By Leo Shartsis and Rodrigo Canga <sup>1</sup>

The surface tension of melts in the system  $\text{ZnO-B}_2\text{O}_3$ , ranging from 0 to 79.5 percent of  $\text{ZnO}$ , were measured with a maximum pull-on-cylinder method. In the two-liquid region, which extends from approximately 0 to 53 percent of  $\text{ZnO}$ , the value of surface tension was that of  $\text{B}_2\text{O}_3$  within the limits of experimental error. With percentages of  $\text{ZnO}$  beyond the two-liquid region, the surface tension value increased rapidly. Melts containing approximately 55 to 65 percent of  $\text{ZnO}$  showed minima in the curves of surface tension versus temperature. Melts containing approximately 65 to 75 percent of  $\text{ZnO}$  had positive temperature coefficients of surface tension. The melt containing 79.5 percent of  $\text{ZnO}$  had a negative temperature coefficient of surface tension. The densities at room temperature were also measured.

## I. Introduction

Zinc oxide and boric oxide are used extensively in glasses, glazes, and enamels. It was considered, therefore, that a study of surface tension in this system of oxides might be of interest in several fields of ceramics. Furthermore, studies of simple systems are not only interpreted more easily but also may be of use in the study of more complex systems.

A further consideration in the selection of the system zinc oxide-boric oxide for study was the expectation of obtaining additional data for the positive temperature coefficients of surface tension. Previous studies [1]<sup>2</sup> had indicated that the phenomenon would probably occur in the present study.

The normal process tending to lower the surface tension as the temperature is raised is generally considered to be associated with the decrease in the force of attraction between adjacent molecules as their average distance of separation increase with rising temperature. The mechanism leading to negative-temperature coefficients of surface tension should always be operative in liquids that have a positive thermal expansion. Any mechanism that operates to give a positive coefficient

must then be considered as superimposed upon the normal tendency.

Two mechanisms have been proposed for explaining the increase in surface tension with increasing temperature. W. A. Weyl [2] postulated that this phenomenon is caused by the presence of asymmetrical groups in the surface of the melt as based upon the observed positive temperature coefficients of surface tension of some glasses high in  $\text{PbO}$  and of fused  $\text{B}_2\text{O}_3$ . These groups tend to orient themselves so that the surface energy is a minimum. As the temperature is increased, the increase in the thermal agitation of the asymmetrical groups produces a decrease in the effective asymmetry, thus raising the surface tension.

Another mechanism, first proposed by Worley [3], depends upon the concentration changes taking place in the surface of a liquid as its temperature is raised. If the surface concentration of a component that depresses the surface tension of the liquid decreases with increasing temperature, the effect is to counteract the normal decrease in surface tension. This counteraction, depending on the magnitude of the effect, may cause the coefficient to become less negative, attain a zero value, or even to become positive. On the other hand, an increase in the surface concentration of the capillary active component with rise in temperature should result in an intensification of the negativity of the coefficient of the test liquid.

<sup>1</sup> Instituto de Optica. Consejo Superior de Investigaciones Cientificas, Madrid, Spain. Guest worker at the National Bureau of Standards 1948-49.

<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

An important point to note is that, according to this mechanism, the coefficient of the pure capillary active substance does not determine the coefficient of the solution. Thus, although phenol and water each have negative coefficients, some of their mixtures have positive ones, and molten PbO and molten  $B_2O_3$  have positive coefficients, whereas some of their molten mixtures have negative ones. Pure substances such as  $B_2O_3$  and PbO, which have positive coefficients, are molecularly complex according to this theory.

Worley's concepts were applied to the data obtained with the systems PbO- $B_2O_3$  and PbO-SiO<sub>2</sub> [1]. The slope of the curve for surface tension versus concentration of PbO,  $[\Delta\sigma/\Delta c]_s$ , was estimated at several temperatures from the data on the surface tension of the system PbO- $B_2O_3$  for a composition containing 85 percent of PbO (table 1). It will be noted that for this liquid the slope is negative. This implies that the surface contains more PbO than the interior of the liquid according to the Gibbs adsorption isotherm [4]. The absolute value of the concentration coefficient is a measure of excess PbO that decreases as the temperature is raised and becomes zero at 900° C, at which temperature the concentration of PbO in the surface is the same as in the interior of the liquid. Since an increase in the PbO content lowers the surface tension of this liquid, the decrease in PbO concentration in the surface resulting from increase in its temperature raises the surface tension, therefore, this liquid has a positive temperature coefficient of surface tension.

TABLE 1. Change of concentration coefficient of surface tension ( $[\Delta\sigma/\Delta c]_s$ , dynes/cm/percent of PbO) with temperature for some melts in the systems PbO- $B_2O_3$  and PbO-SiO<sub>2</sub> [1].

Percentage of PbO	PbO- $B_2O_3$			
	600° C	700° C	800° C	900° C
85	-1.3	-0.8	-0.3	-0
71	+0	+ .7	+1.3	+1.8

Percentage of SiO <sub>2</sub>	PbO-SiO <sub>2</sub>				
	900° C	1,000° C	1,100° C	1,200° C	1,300° C
6.3	-6.4	-5.6	-5.5	-4.5	-4.1
16.8	-2.9	-2.9	-2.8	-2.8	-2.7

It is interesting to apply the same type of reasoning to the melt that contains approximately 71 percent of PbO (table 1). The concentration coefficient of surface tension is positive, implying that there is less PbO in the surface than in the interior, and the value of the coefficient is a measure of the amount of this deficiency. Since the coefficient rises with increasing temperature, the concentration of PbO must decrease as the temperature rises. In this concentration region, however, PbO raises the surface tension and, therefore, decrease of PbO in the surface must result in a lowering of the surface tension and a resultant negative temperature coefficient of surface tension, even though both components of this solution themselves have positive coefficients. Thus, both negative and positive temperature coefficients in this system are accompanied by appropriate concentration changes in the surface of the liquid.

In the system PbO-SiO<sub>2</sub> [1], the temperature coefficients of surface tension are positive in the low silica range and become smaller as the silica content is increased until they approach zero at about 30 to 35 percent of silica. Increasing the amount of PbO lowers the surface tension in this composition range and, therefore, there must be an excess of PbO in the surface. Judging by the decrease in the magnitude of the concentration coefficients with increasing temperature (table 1), the concentration of PbO in the surface decreases as the temperature is raised.

## II. Phase Equilibrium Relations

Figure 1 shows the phase-equilibrium diagram [5] of the system ZnO- $B_2O_3$ . A region of liquid immiscibility extends from almost zero to about 53 percent of ZnO.<sup>3</sup> Previous experience [1] has shown that in this region the value of surface tension obtained is that of the upper liquid. In this investigation the upper liquid is almost pure  $B_2O_3$ . From the two-liquid region to about 68 percent of ZnO the liquidus curve,  $1,000 \pm 3^\circ$  C, is very flat even though a compound exists in this region. It was expected that in this region clear glasses could be obtained. Above 68 percent of ZnO the liquidus temperature rises rapidly with increasing amounts of ZnO, and it is to be expected that the glass-forming tendency would be restrained because of the rapid crystallization of the melts.

<sup>3</sup> All compositions are expressed as weight percent.

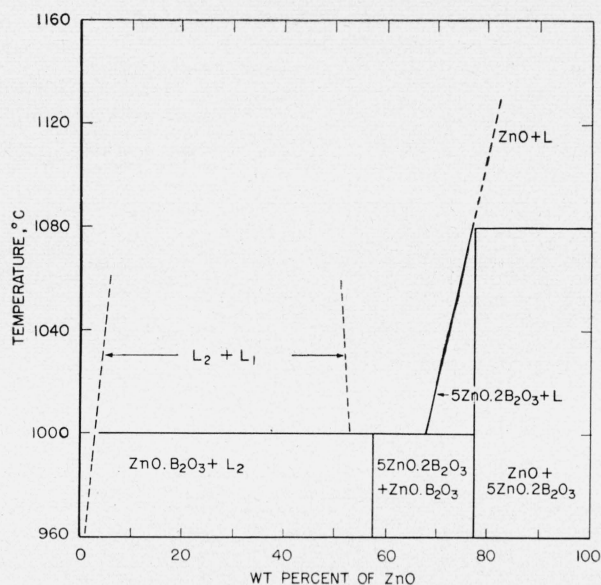


FIGURE 1. Phase equilibrium diagram of the system ZnO-B<sub>2</sub>O<sub>3</sub> [5].

### III. Preparation of Melts and Methods of Test

#### 1. Preparation of Melts

The liquids investigated were made by melting in platinum crucibles the requisite amounts of chemically pure zinc oxide and boric acid. The melts, weighing from 300 to 500 g, were stirred with a motorized propellor-type platinum stirrer and, when they seemed homogeneous, were poured into iron molds. Melts containing more than 65 percent of ZnO crystallized while cooling, and even that containing 65 percent showed traces of devitrification.

In order to obtain a clear glass containing the smallest amount of ZnO possible in this system, a preparation containing about 52.5 percent of ZnO was prepared. When cooled, the product had an opalescent coating representing the upper layer that was removed readily by immersing in hot distilled water for a few minutes.

#### 2. Chemical Analysis

Samples from each melt were analyzed for ZnO by a triple evaporation with HF and H<sub>2</sub>SO<sub>4</sub>. Analyses were made also of many of the samples remaining from the individual determinations of surface tension.

### 3. Measurement of Surface Tension

The method [6] of measuring surface tension was that of determining the maximum pull exerted on a thin-walled platinum cylinder when its lower edge was in contact with the test liquid. In general, the first determination of surface tension of any melt was made at 1,300° C. Subsequent measurements were made at 100-deg C intervals of decreasing temperature until the glass was too viscous to yield in a reasonable time or until crystallization had occurred. In several instances, however, this schedule was altered in order to determine the effect of such a change on the character of the temperature coefficient of surface tension. Tests on the same melt at different temperature schedules are often not comparable, a phenomenon that has been noted before [6].

### 4. Measurement of Density

In order to obtain accurate values of surface tension with the method adopted, it is necessary to know the density of the liquid at the temperature of test. Great accuracy, however, is not necessary, as an error of 10 percent would, in general, cause an error of about 0.5 percent in the values of surface tension. The densities of the solid compositions were measured by determining the buoyant effect of distilled water. To convert the densities at room temperature to those at 1,000° C, 0.2 was subtracted from each value, because experience has shown that with many glasses the average decrease in density from room temperature to 1,000° C is about 0.2.

## IV. Results and Discussion

#### 1. Analytical Results

The analytical results are given in the last two columns of table 2. With two exceptions, the percentages of ZnO obtained after surface tension determinations were a little higher than those corresponding to the original preparations. The differences in no case, however, exceed 0.3 percent.

#### 2. Reproducibility of Surface Tension Data

The values of surface tension are given in table 2. Inspection of this data shows that the agreement between the surface tension results of duplicate melts was poor when the schedules of tem-



TABLE 2. Surface tension, density, and chemical analysis of some compositions in the system ZnO-B<sub>2</sub>O<sub>3</sub>

Accepted percentage of ZnO	Determination number	Surface tension, dynes/cm, at—							Percentage of ZnO by analysis		
		1,400° C	1,300° C	1,200° C	1,100° C	1,000° C	900° C	800° C	Density at approximately 25° C	Before surface-tension measurement	After surface-tension measurement
0.....		97.2	93.6	90.1	86.5	83.0	79.5	75.9			
10.....	1		95.2	91.1	86.5	82.0	78.4				
50.....	1			90.9							
	2				87.9	83.2	79.7				
55.0.....	1		153.8	143.6	137.4	138.2			3.37	55.0	
	a 2				133.5	135.0	141.8				
56.1.....	1		162.7	157.0	150.2	151.0	159.9		3.42	56.1	56.4
	a 2				144.2	147.9	156.5				56.1
58.6.....	1		184.4	181.8	179.4	180.0	185.2	b [195.5]	3.48	58.6	58.8
	2		185.8	180.2	177.9	178.9	183.5	[191.3]			58.9
	a 3				174.5	175.9	178.7	[189.5]			
60.8.....	1		208.0	203.6	201.3	201.0	203.2		3.56	60.8	
	2		205.6	204.5	201.6	201.0	203.8				
64.6.....	1		237.8	235.2	232.5	232.1	234.7		3.68	64.6	
	a 2			236.6	234.1	234.5	235.4				64.6
65.6.....	1		250.0	246.6	244.2	242.0	[239.7]		3.70	65.6	65.7
	2		250.5	245.8	243.8	242.5					
	1		286.8	285.2	281.5	277.0				70.5	70.7
70.6.....	2		287.1	285.7	283.4	280.3					70.2
	3		289.7	286.5	283.4	278.7					
74.6.....	1		321.6	318.9	314.7				c 4.02	74.6	
	2		321.8	319.3	315.6						
79.5.....	1	355.3	355.9	360.3					c 4.22	79.6	79.5
	2	353.3	354.2								

a Not on regular temperature versus time schedule.

b Figures in brackets are extrapolated values.

c Crystallized.

perature were varied. However, the magnitude only, and not the algebraic sign of the temperature coefficient of surface tension, was dependent on the schedule.

The dependence of the surface-tension results obtained upon the thermal treatment of the melt can be traced to several factors, among which are:

(1) The slowness with which the equilibrium between the surface layer and the interior of the liquid is adjusted,

(2) The presence of bubbles in the melt, and the

(3) Volatilization, which affects the equilibrium between the surface and the interior and, in addition, may cause some material to condense on the upper portion of the cylinder and its supporting wire.

### 3. Surface Tension Minima

Figure 2 shows, in graphical form, the surface-tension results obtained when the previously described schedules of making observations was maintained. A point of interest is the appearance of minima in the curves for liquids that

contain between 55 and 65 percent of zinc oxide. The behavior of solutions of phenol and water [3], with regard to the change of surface tension with increase in temperature, is similar to that of the system ZnO-B<sub>2</sub>O<sub>3</sub>. The more concentrated solutions also exhibit minima in the surface tension versus temperature curves. This phenomenon points to two competing mechanisms; one tends to decrease the surface tension and the other to increase it with an increase in temperature.

### 4. Region Above 65 Percent of ZnO

The measurements of surface tension below the liquidus temperature of these liquids was impossible because of the strong tendency of the melts in this region of composition to crystallize. This onset of crystallization was observed by the decrease in the values of surface tension as the melt was maintained at a constant temperature. The crystalline material, apparently denser than the melt, sank and there remained a liquid with a surface tension value lower than that of the original melt.

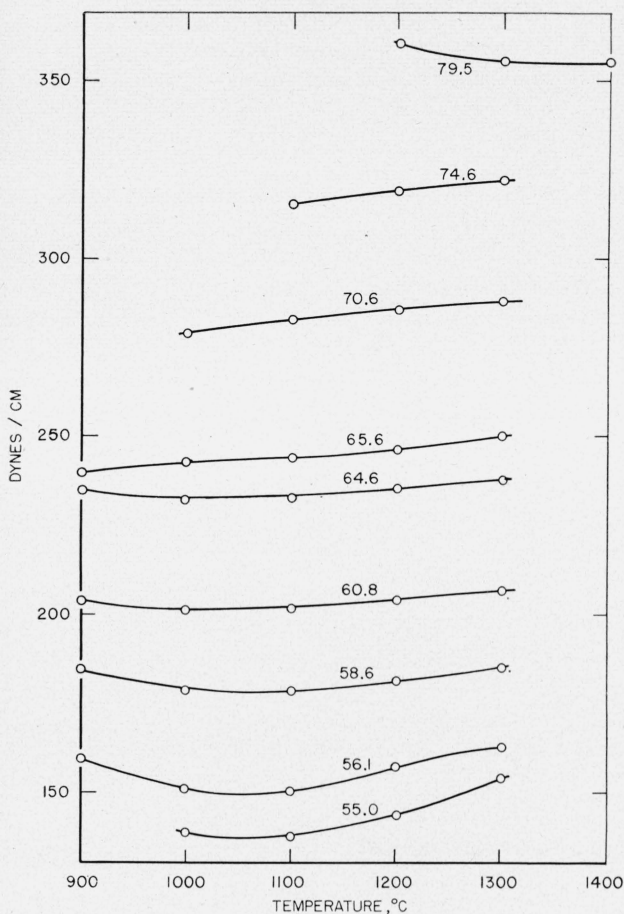


FIGURE 2. Surface tension of melts in the system ZnO-B<sub>2</sub>O<sub>3</sub> as a function of temperature.

The percentage of ZnO is shown just above each curve.

With the exception of the liquid containing 79.5 percent of ZnO, the temperature coefficient of surface tension of melts in this region was positive.

### 5. Effect of Composition

A plot of surface tension values at 1,200° C against the percentages of ZnO is shown in figure 3. in the two liquid region extending from almost pure B<sub>2</sub>O<sub>3</sub> to about 53 percent of ZnO the surface tension is that of the upper liquid, which is known to be practically pure B<sub>2</sub>O<sub>3</sub>. The first measurements, determined for a melt containing 50 percent of zinc oxide, were very erratic, and successive measurements at the same temperature resulted in unexpected differences in surface tension values of about 20 dynes/cm. Further investigation revealed that this erratic behavior was due to an

extremely thin upper layer and, because of this, the bottom edge of the cylinder sometimes contacted the lower layer and gave relatively high values. If great care was exercised in contacting only the upper layer, correct results could be obtained.

Above the two-liquid region, the values of surface tension rise rapidly with increasing amounts of ZnO. According to the Gibbs adsorption isotherm, this indicates that the concentration of ZnO in the surface is less than that in the body of the liquid. This is one factor that would operate to cause a greater loss of B<sub>2</sub>O<sub>3</sub> than of ZnO in melts heated at high temperatures as indicated by the analytical results (table 2). In addition, the greater volatility of B<sub>2</sub>O<sub>3</sub> as compared to ZnO should also result in an increase in the ZnO content of melts heated at high temperatures.

## V. Summary

The surface tension values of zinc borate melts were practically constant within the two-liquid region extending from about zero to 53 percent of ZnO and that of B<sub>2</sub>O<sub>3</sub>. With percentages of ZnO beyond the two-liquid region, the surface-tension values increased rapidly with increasing ZnO content. With one exception, melts of all composi-

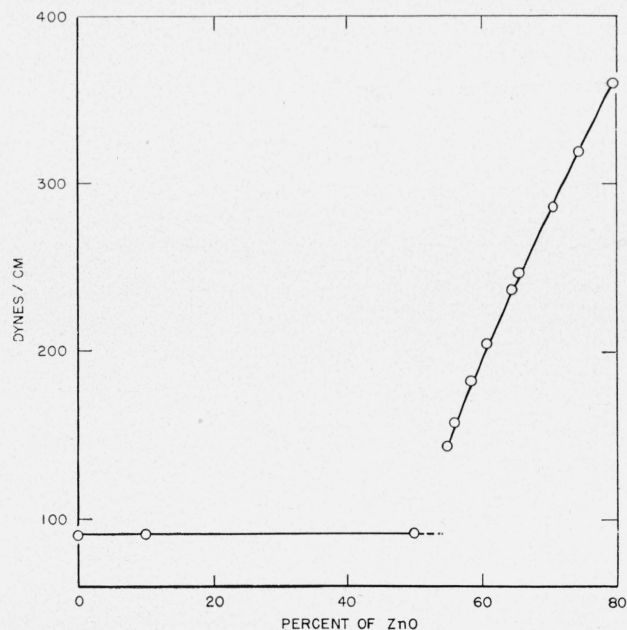


FIGURE 3. Surface tension of melts in the system ZnO-B<sub>2</sub>O<sub>3</sub> at 1,200° C as a function of the percentage of ZnO.

tions had positive temperature coefficients of surface tension, and those containing 55 to 65 percent of ZnO showed minima in the curves of surface tension versus temperature. Two theories regarding the cause of positive temperature coefficients of surface tension were reviewed.

## VI. References

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